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(54) PROCESS FOR PREPARING SILVER CARBOXYLATES

(71) We, FUJI PHOTO FILM CO., LTD., a Japanese Company, of No. 210, Nakanuma, Minami/Ashigara-Shi, Kanagawa, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

5 This invention relates to a process of preparing a silver carboxylate and in particular to a process for the preparation of fine particles of a silver carboxylate which can advantageously be used in the manufacture of heat-developable photographic materials. 5

10 The use of silver carboxylates as heat-developable photographic materials has been described in, for example, U.S. Patents Nos. 3,152,904, 3,457,075, 3,589,901 and 3,589,903. These heat-developable photographic materials essentially consist of, for example, a silver carboxylate such as silver behenate, a photo-sensitive silver halide or a compound which can produce a photo-sensitive silver halide after reaction with the silver carboxylate, and a reducing agent. After these heat-developable photographic materials are imagewise exposed and then heated, silver images are formed by the reaction of silver carboxylate and reducing agent which is catalysed by the sensitized silver halide. 10 15

15 For the preparation of silver carboxylates which are suitable as these heat-developable photographic materials, a method as disclosed in U.S. Patent No. 3,458,544, is known where a solution of a carboxylic acid in a water-insoluble solvent is admixed with an aqueous solution of an alkali-soluble silver complex to form fine oily particles of silver carboxylate dispersed in water. However when heat-developable photographic materials as aforescribed are prepared with silver carboxylates prepared according to this method, images can apparently be obtained after exposure and heat development, but the value of the Dmax/coated silver content is low and fog tends to occur. Thus, the use of these silver carboxylates is defective in this respect. 20

25 An object of this invention is to provide a process for the preparation of fine particles of silver carboxylates, which silver carboxylates can be used to make heat-developable photographic materials which at least partially overcome the aforementioned defects in the use of conventional silver carboxylates. 25

30 According to the present invention there is provided a process of preparing a silver carboxylate, comprising emulsifying, in an aqueous phase, by the action of ultrasonic radiation, a solution of a carboxylic acid dissolved in an organic solvent which dissolves the carboxylic acid, but does not substantially dissolve the silver carboxylate or silver nitrate and is sparingly soluble in water, and mixing the emulsion so formed with an aqueous solution of an alkali-soluble silver complex. 30

35 The fine silver carboxylate particles so prepared can advantageously be used as materials in the manufacture of heat-developable photographic materials. Thus, when the carboxylate fine particles are used for these photographic materials, the value of the Dmax/coated silver content is extremely high, and further, the occurrence of fog is extremely small after their heat-development. 35

40 The method of the present invention produces fine particles of silver carboxylates having a particle size ranging from 0.02 micron to 10 microns, preferably 0.1 micron to 0.5 micron, and which can satisfy the aforescribed object of this invention. 40

45 The term "emulsification" means, in general, that semi-stable state in which a liquid is dispersed in another liquid in the form of numerous droplets and various methods are known for the production of such a state. In order to adjust the diameter of the droplets in an emulsion to a desired size, two different methods have generally been used. One method is the so-called "condensation method" where starting nuclei of extremely small diameter are allowed to 45

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grow to droplets of the desired size, and the other method is the so-called "dispersion method" where droplets of large size are divided into droplets of small size. In general, emulsification using the latter dispersion method is used industrially and is often performed by using a shaker, a mixer, a colloid-mill, a homogenizer or ultrasonic irradiation. All of these emulsification methods other than those using ultrasonic waves are in general carried out using a surfactant. On the other hand, the emulsification by ultrasonic methods has the characteristic that a concentrated and well dispersed emulsion can be prepared without the use of any surfactant (cf. *Emulsion Science* written by P. Sherman, Academic Press (1968)).

It is preferred that the preparation of silver carboxylates to be used for the manufacture of heat-developable photographic materials does not leave impurities in the product. This is because the properties of photographic materials are often markedly impaired by impurities contained in the raw materials used for the preparation of these photographic materials.

For example, when the silver carboxylates prepared according to the method described in U.S. Patent No. 3,458,544 (see column 3, lines 6-18, where cationic surfactants, especially those having a halogen ion, or anionic surfactants, are used for emulsification) are used as raw materials for heat-developable photographic materials, fog often appears on heat development and an image having a sufficiently high value of D_{\max} /coated silver content cannot be produced.

However, when silver carboxylates, which are prepared using ultrasonic waves (without any surfactant) for the emulsification, are used as the raw materials of heat-developable photographic materials, fog hardly appears on heat development and images having a high value of D_{\max} /coated silver content can be produced.

The frequency of the ultrasonic waves which can be used in this invention is preferably in the range of 10 KHz to 10 MHz, more preferably in the range of 15 KHz to 500 KHz. Ultrasonic waves of low frequency are suitable for emulsification, but those which fall in the range of audible sonic waves are too low since strong sonic waves of a low frequency cause human physical discomfort; this factor therefore determines the lower limit of the frequency. The upper limit to the usable frequency is determined by the fact that, if the frequency is too high, the efficiency of emulsification is reduced.

The range of energy of ultrasonic waves which can be used in the present invention is from 0.05 to 10^4 W/cm², preferably 0.1 to 10^3 W/cm². If the energy is too low, the efficiency of emulsification is poor, and therefore, this factor determines the lower limit of this energy. The higher the energy of the ultrasonic waves, the higher the cost of the apparatus used. The upper limit of the energy is therefore determined only from the standpoint of economics.

When a carboxylic acid solution is treated with ultrasonic radiation in the presence of an aqueous phase, it is emulsified after a short time, viz. from about 30 seconds to 60 minutes, more generally, 3 minutes to 30 minutes.

In the process of the present invention, an ultrasonic oscillator of any type can be used, including, for example, an oscillator actuated by piezoelectric effects, an oscillator actuated by magnetostriction effects or a liquid-spouting oscillator actuated by a liquid pipe.

Carboxylic acids whose silver salts are relatively stable to light are suitable for the present invention. Representative examples of suitable carboxylic acids are long-chain aliphatic carboxylic acids having 10 or more carbon atoms, e.g. up to about 24 carbon atoms, and having preferably 10 to 22 carbon atoms, such as capric acid, lauric acid, myristic acid, palmitic acid, stearic acid or behenic acid.

The organic solvent used for the silver carboxylates is one which can dissolve the carboxylic acid, but does not substantially dissolve the silver carboxylate and silver nitrate and is sparingly soluble in water. Examples of suitable solvents are the esters of alcohols, e.g. such alcohols which have from 1 to 8 carbon atoms, or phenols, e.g., those having from 6 to 12 carbon atoms, with phosphoric acid, phthalic acid or carboxylic acid, which esters have, for example, from 1 to 12 carbon atoms and are liquid at room temperature (about 20 to 30°C). Other suitable solvents are aromatic hydrocarbons, e.g., those having from 6 to 12 carbon atoms.

Typical examples of such solvents are: tricresyl phosphate, tributyl phosphate, monoctyl-dibutyl phosphate, dimethyl phthalate, dioctyl phthalate, dimethoxyethyl phthalate, amyl acetate, isoamyl acetate, isobutyl acetate, isopropyl acetate, ethyl acetate, 2-ethylbutyl acetate, butyl acetate, propyl acetate, dioctyl sebacate, dibutyl sebacate, diethyl sebacate, diethyl succinate, ethyl formate, propyl formate, butyl formate, amyl formate, ethyl valerate, diethyl tartrate, methyl butyrate, ethyl butyrate, butyl butyrate, isoamyl butyrate, toluene and xylene.

The preferred alkali-soluble silver complex is a silver-ammonia complex. In addition, other alkali-soluble silver complexes having a larger solubility product than that of the silver carboxylates to be prepared, for example, silver-amine complexes (such as silver-ammonia complex of methylamine or ethylamine) can be used. The pH of the aqueous solution of silver complex is preferably 5 or more, e.g., from 5 to 14, preferably from 9 to 12. If the pH of the solution is lower than 5, the yield of the silver carboxylate prepared is poor. A suitable concentration of the silver complex is from 0.01 N to 6 N, preferably from 0.1 N to 4 N.

Distilled water is generally used as the aqueous phase to emulsify the oil phase in which the carboxylic acid is dissolved, or else an aqueous solution of nitric acid, perchloric acid, formic acid, acetic acid or a like acid can be used. A suitable concentration in the oil phase of the carboxylic acid which can be used is from 0.2 wt. % to 50 wt. %, preferably from 1 wt. % to 30 wt. % with a molar ratio of the silver complex to the carboxylic acid of from 0.3: 1 to 1: 1, preferably 0.5: 1 to 0.9: 1. The pH of the aqueous phase is preferably 9 or less, e.g., 0 to 8, preferably 1 to 6. If the pH of the aqueous phase in the formation of the silver carboxylates is too high, the resulting carboxylate products have the defect that fog tends to occur readily during heat development of the heat-developable photographic materials produced with these carboxylate products.

The reaction temperature of the process of this invention can be freely selected. However, use of a reaction temperature which is too high has the disadvantage that the solvent tends to boil. In general, a suitable reaction temperature is from -10°C to 80°C , preferably from 0°C to 60°C . The solution concentration, stirring condition and mixing speed, can be varied as desired.

The ratio by volume of the aqueous phase to the oil phase containing the carboxylic acid is suitably from 1: 3 to 10: 1, more preferably from 1: 1 to 4: 1.

The process for the preparation of silver carboxylates preferably comprises the following steps:

- (1) The carboxylic acid is dissolved in one of the aforescribed solvents.
- (2) The resulting solution is treated with ultrasonic waves in the presence of an aqueous phase as hereinbefore described.
- (3) The silver complex aqueous solution is admixed with the solution as treated in the above step (2). (This admixture can be carried out simultaneously with the treatment with ultrasonic waves if desired.)
- (4) The precipitates of the silver carboxylate are separated. (In this separation, any conventional method can be employed, for example, decantation, filtration or centrifuging.)
- (5) The water-soluble residues (for example, silver nitrate or nitric acid) are washed out with water.
- (6) The thus washed precipitates are further washed with a solvent which can form a homogeneous phase with the solvent of the carboxylic acid and can dissolve the carboxylic acid (for example, methanol, ethanol, isopropanol or propanol).

Heat-developable photographic materials which can be produced with the fine crystals of silver carboxylate so prepared are those comprising the following elements (1), (2), (3) and (4) on a support: (1) fine crystals of a silver carboxylate prepared according to the process of this invention, (2) a catalytic amount of a photo-sensitive silver halide or a compound which can form a photo-sensitive silver halide after reaction with a silver carboxylate, (3) as a reducing agent, a compound which can reduce the silver carboxylate to form silver images, when heated in the presence of the sensitized silver halide, and (4) a binder, for example, a binder as described in U.S. Patent No. 3,589,903.

The heat-developable photosensitive layer can further contain the following additives: blackening agents to darken further the image obtained, as disclosed in U.S. Patents Nos. 3,080,254 and 3,107,174, for example, mercapto compounds, azole-thions and phthalazinones; development accelerators, for example, carboxylic acids or compounds which can display a basic character after being heated, such as oxalic acid-amine salt; inorganic hydroxides; reducing agents such as photolytic reducing agents, for example, a compound such as diphenyldiketone which can accelerate the photolysis of ascorbic acid ester when the ester is used; as well as spectral sensitizing dyes to impart sensitivity, and sensitize the photo-sensitive layer to light of a long wavelength, for example, mero-cyanine dyes, rhodacyanine dyes, acid dyes and cyanine dyes which contain thiohydantoin nuclei or rhodanine nuclei, for example, dyes as disclosed in U.S. Patents Nos. 3,457,075 and 3,761,279.

In heat-developable photographic materials, for example as described in Japanese Patent Publication Nos. 22185/70, 41865/71 and 4924/68 and U.S. Patents Nos. 3,589,901 and 3,589,903, it has been found that, when the fine particles of silver carboxylate produced by the process of the present invention are used as the organic silver salts, the value of the D_{max} /coated silver content increases and there is hardly any fog caused by heat during development.

The increase in the value of D_{max} /coated silver content means that a smaller amount of silver salt is required for forming images of the same density, and consequently, a reduction of manufacturing cost can be expected therefrom. The decrease in fog during heat development means that the development time can easily be extended so that, for example, there is the advantage that any insufficient exposure can easily be complemented by prolonging the time of heat development. A further advantage is that a background of a more preferable whiteness can be obtained. These advantages are very significant in the manufacture and use of heat-developable photographic materials.

The invention will now be illustrated with reference to the following Examples. Unless otherwise indicated, all percentages are by weight.

EXAMPLE 1

3.4 g of behenic acid were dissolved in 100 ml of tricresyl phosphate at 60°C, and the temperature of the resulting solution was reduced to 45°C. 100 ml of distilled water at 45°C were added to this solution, and the resulting solution was subjected to ultrasonic irradiation of 20 KHz and 45 W for 10 minutes in an ultrasonic apparatus (UR-150 P, manufactured by the Tominaga Manufacturing Co.) to prepare an oil-in-water emulsion.

Next, aqueous ammonia was added to about 80 ml of an aqueous solution containing 1.7 g of silver nitrate to form a silver-ammonium complex, and water was added thereto to increase the volume of the aqueous solution to 100 ml (adjusted to 45°C). This solution of complex was then added, with stirring, to the emulsion obtained in the previous step. The silver salt was separated by filtration, and then 400 ml of distilled water were added thereto to wash the salt. This washing was repeated three times and then 400 ml of methanol were added for further washing. Finally, the silver behenate formed was separated by centrifuging, whereby 3.7 g of silver behenate were obtained, and designated "Silver Behenate A".

Independently of the above preparation, another sample of silver behenate was prepared in the same manner as the aforescribed procedure except that the mixture was vigorously stirred (at a stirring speed of about 800 r.p.m.) instead of being treated with ultrasonic radiation. Thus, 3.8 g of silver behenate were obtained, and designated "Silver Behenate B".

Next, two kinds of heat-developable photographic composition, as shown in the following Table 1, were prepared, one using Silver Behenate A, and the other using Silver Behenate B, and each of these was applied to a polyethylene terephthalate film support to produce two kinds of heat-developable photographic material.

TABLE 1

Polymer dispersion of silver behenate A or B*	40 ml
Solution of 0.9 g of zinc bromide, 0.1 g of zinc iodide and 0.2 g of mercuric bromide dissolved in 20 ml of methanol	1.2 ml
Acetone solution containing 0.02 wt. % benzoxazolylidene-thiohydantoin sensitizing dye	1 ml
2,2'-Methylenebis (6- <i>t</i> -butyl-4-methylphenol) (25 wt. % methoxy-methanol solution)	8 ml
Ethoxy-methanol solution containing 10 wt. % phthalazinone	8 ml

* Preparation of the silver behenate-polymer dispersion: 5 g of silver behenate A or B were added to 40 ml of an isopropyl alcohol solution containing 4 g of polyvinyl butyral and the mixture was treated in a ball-mill for 4 hours to form a dispersion.

The photographic material prepared in this way was exposed using a tungsten lamp through a transparent negative original having gradations, and was then heated at 120°C for 10 seconds, whereby a positive image having gradations was formed. The resulting values of Dmax obtained are shown in the following Table 2. In addition, the heating time at 120°C necessary to produce a fog of 0.08 density was measured in each of these two kinds of photographic material. These fogging results obtained are also shown in Table 2.

TABLE 2

	Silver Behenate A	Silver Behenate B
Coated silver content	1.1 g/m ²	1.3 g/m ²
Dmax	1.4	0.6
Time until occurrence of fog of 0.08 density	50 sec.	22 sec.

As is evident from the results contained in the above Table 2, the value of Dmax/coated silver content is larger and the occurrence of fog is suppressed in the material prepared using Silver Behenate A as compared with the material prepared using Silver Behenate B.

EXAMPLE 2

11 g of lauric acid were dissolved in 100 ml of isoamyl acetate at 60°C and the temperature of the resulting solution was reduced to 20°C. 100 ml of distilled water at 20°C were added to this solution, and the resulting solution was subjected to ultrasonic irradiation of 20 KHz and 45 W for 10 minutes in an ultrasonic apparatus (UR-150 P produced by the Tominaga Manufacturing Co.) to prepare an oil-in-water emulsion.

Next, 8.5 g of silver nitrate were dissolved in about 80 ml of distilled water and aqueous ammonia was added thereto to form a silver-ammonium complex, and thereafter, distilled water was added thereto to increase the total volume of aqueous solution (adjusted to 20°C) to 100 ml. This solution of complex was then added, with stirring, to the emulsion obtained in the previous step. The silver salt was separated by filtration, and then 400 ml of distilled water was added thereto for washing. This washing was repeated three times, and then 400 ml of methanol were added for further washing. Finally, the fine crystals of silver laurate so formed were separated by centrifuging, whereby 15 g of silver laurate were obtained, and designated "Silver

Laurate A".

Independently of the above preparation, other silver laurate crystals were prepared in the same manner as the aforescribed procedure except that the mixture was vigorously stirred (at a stirring speed of about 800 r.p.m.) instead of being treated with ultrasonic waves. Thus, 14.6 g of silver laurate were obtained, and designated "Silver Laurate B".

Two kinds of heat-developable photographic compositions consisting of the components shown in the following Table 3 were prepared, one using the Silver Laurate A and the other using Silver Laurate B, and each of these was applied to a polyethylene terephthalate transparent film support to produced two kinds of heat-developable photographic material.

TABLE 3

Polymer dispersion of silver laurate*	45 ml
Solution of 4 g of ammonium bromide and 0.5 g of mercuric bromide dissolves in 100 ml of methanol	0.8 ml
Methanol solution of 0.025 wt. % tetrachlorotetrabromo-fluorescein acid dye	0.6 ml
Phthalazinone (5 wt. % ethoxy methanol solution)	1.2 ml
p-Phenylphenol (70 wt. % ethoxy methanol solution)	8 ml

* Preparation of silver laurate-polymer dispersion: 5 g of silver laurate A or B were added to 40 ml of an isopropyl alcohol solution containing 4 g of polyvinyl butyral and the mixture was treated in a ball-mill for 4 hours to form a dispersion.

The photographic material so produced was exposed using a tungsten lamp through a transparent negative original having gradations, and was then heated at 120°C for 5 seconds, whereby a positive image having gradations was formed. The resulting values of Dmax obtained are shown in the following Table 4. In addition, the heating time necessary to produce at 120°C a fog of 0.08 density was measured for each of these two kinds of photographic material. Their fogging results obtained are also shown in the Table 4.

TABLE 4

	Silver Laurate A	Silver Laurate B
Coated silver content	1.2 g/m ²	1.3 g/m ²
Dmax	1.5	0.7
Time until occurrence of fog of 0.08 density	30 sec.	13 sec.

As is evident from the results contained in Table 4 above, the value of the Dmax/coated silver content is larger and the occurrence of fog is suppressed in the material prepared using Silver Laurate A as compared with the material prepared using Silver Laurate B.

EXAMPLE 3

10 g of lauric acid were dissolved in 100 ml of isoamyl butyrate at 60°C and the temperature of the resulting solution was reduced to 40°C. 100 ml of distilled water at 40°C were added thereto, and the resulting solution was subjected to ultrasonic irradiation of 20 KHz and 45 W for 15 minutes in an ultrasonic apparatus (UR-150 P produced by the Tominaga Manufacturing Co.) to prepare an oil-in-water emulsion.

Next, 8.5 g of silver nitrate were dissolved in about 80 ml of distilled water and aqueous ammonia was then added thereto to form a silver-ammonium complex, and thereafter, distilled water was added thereto to increase the total volume of the aqueous solution (adjusted to 200 ml). This solution of complex was then added, with stirring, to the emulsion obtained in the above step. The silver salt so produced was separated by filtration, and then 400 ml of distilled water was added thereto for washing. This washing was repeated three times, and then 400 ml of methanol were added for further washing. Finally, the fine crystals of silver laurate so formed were separated by centrifuging, whereby 14.1 g of silver laurate were obtained, and designated "Silver Laurate C".

Independently of the above preparation, another silver laurate was prepared in the same way as the aforescribed procedure except that 100 ml of a 1 wt. % cetyl-pyridinium bromide (surfactant) aqueous solution were added to the lauric acid dissolved in isoamyl butyrate, in place of the 100 ml of distilled water. Thus, 14.9 g of silver laurate were obtained, and designated "Silver Laurate D".

Two kinds of heat-developable photographic compositions consisting of the components shown in Table 3 were prepared, one using Silver Laurate C, and the other using Silver Laurate D, and each of these was applied to a polyethylene terephthalate transparent film support to product two kinds of heat-developable photographic material.

Each of these photographic materials was exposed using a tungsten lamp through a transparent negative original having gradations, and was then heated at 120°C for 5 seconds, whereby a positive image having gradations was formed. The Dmax was 1.2 when Silver Laurate C was used and the Dmax was 0.4 when Silver Laurate D was used. The coated silver content of each of these two photographic materials was almost the same.

This result shows that, in a process for preparing silver carboxylates to be used in heat-

developable photographic materials, the use of a surfactant is inferior to the use of ultrasonic irradiation in the present invention in that an image formed in the material prepared using the former method has a smaller value of Dmax/coated silver content than an image formed in the material prepared using the latter method.

5 WHAT WE CLAIM IS:—

1. A process of preparing a silver carboxylate, comprising emulsifying, in an aqueous phase, by the action of ultrasonic radiation, a solution of a carboxylic acid dissolved in an organic solvent which dissolves the carboxylic acid, but does not substantially dissolve the silver carboxylate or silver nitrate and is sparingly soluble in water, and mixing the emulsion so
10 formed with an aqueous solution of an alkali-soluble silver complex.
2. A process as claimed in Claim 1, wherein the frequency of said ultrasonic radiation is from 10 KHz to 10 MHz.
3. A process as claimed in Claim 2, wherein said frequency is from 15 KHz to 500 KHz.
4. A process as claimed in any preceding claim, wherein the energy of said ultrasonic
15 radiation is from 0.05 to 10⁴ W/cm².
5. A process as claimed in Claim 4, wherein said energy is from 0.1 to 10³ W/cm².
6. A process as claimed in any preceding claim, wherein the time of the treatment with said ultrasonic radiation is from 30 seconds to 60 minutes.
7. A process as claimed in Claim 6, wherein the time is from 3 minutes to 30 minutes.
8. A process as claimed in any preceding claim, wherein said carboxylic acid is an aliphatic
20 carboxylic acid having 10 or more carbon atoms.
9. A process as claimed in Claim 8, wherein the carboxylic acid has from 10 to 22 carbon atoms.
10. A process as claimed in any preceding claim, wherein said carboxylic acid is capric acid, lauric acid, myristic acid, palmitic acid, stearic acid or behenic acid.
11. A process as claimed in any preceding claim, wherein the concentration of the carboxylic
25 acid is from 0.2 wt. % to 50 wt. %.
12. A process as claimed in Claim 11, wherein the concentration is from 1 wt. % to 30 wt. %.
13. A process as claimed in any preceding claim, wherein said solvent is an ester of an alcohol or a phenol with phosphoric acid, phthalic acid or a carboxylic acid, which ester is
30 liquid at room temperature, or an aromatic hydrocarbon.
14. A process as claimed in Claim 13, wherein said alcohol has from 1 to 8 carbon atoms, said phenol has from 6 to 12 carbon atoms, said carboxylic acid has from 1 to 12 carbon atoms and said aromatic hydrocarbon has from 6 to 12 carbon atoms.
15. A process as claimed in any preceding claim, wherein said solvent is tricresyl phosphate, tributyl phosphate, mono-octyl-dibutyl phosphate, dimethyl phthalate, dioctyl phthalate,
35 dimethoxyethyl phthalate, amyl acetate, isoamyl acetate, isobutyl acetate, isopropyl acetate, ethyl acetate, 2-ethylbutyl acetate, butyl acetate, propyl acetate, dioctyl sebacate, dibutyl sebacate, diethyl sebacate, diethyl succinate, ethyl formate, propyl formate, butyl formate,
40 amyl formate, ethyl valerate, diethyl tartrate, methyl butyrate, ethyl butyrate, butyl butyrate, isoamyl butyrate, toluene or xylene or a mixture of two or more thereof.
16. A process as claimed in any preceding claim, wherein said alkali-soluble silver complex is a silver-ammonia complex.
17. A process as claimed in any preceding claim, wherein the pH of said silver complex
45 aqueous solution is 5 or more.
18. A process as claimed in Claim 17, wherein the pH is from 9 to 12.
19. A process as claimed in any preceding claim, wherein said aqueous phase is distilled water or an aqueous solution of nitric acid, perchloric acid, formic acid or acetic acid.
20. A process as claimed in any preceding claim, wherein the pH of said aqueous phase is
50 from 0 to 8.
21. A process as claimed in any preceding claim, wherein the pH of said aqueous solution is from 1 to 6.
22. A process as claimed in any preceding claim, wherein the volume ratio of said aqueous phase to said solution containing said carboxylic acid is from 1 : 3 to 10 : 1.
23. A process as claimed in Claim 22, wherein said volume ratio is from 1 : 1 to 4 : 1.
24. A process as claimed in any preceding claim, wherein the reaction temperature is from
55 0°C to 60°C.
25. A process as claimed in any preceding claim, which includes the further steps of: (1) separating the precipitate of said silver carboxylate, (2) washing out the water-soluble residues with water, and (3) washing the thus washed precipitates with a solvent which can
60 form a homogeneous phase with said solvent of said carboxylic acid and can dissolve said carboxylic acid.
26. A process as claimed in Claim 25, wherein the solvent used for washing in stage 3 is methanol, ethanol, isopropanol or propanol.
27. A process for preparing silver carboxylates as claimed in Claim 1, substantially as
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hereinbefore described with reference to any one of Examples 1 to 3.

28. A silver carboxylate which has been prepared by a process as claimed in any preceding claim.

5 29. A heat-developable photographic material comprising on a support: (1) fine crystals of a silver carboxylate as claimed in Claim 28, (2) a catalytic amount of a photosensitive silver halide or a compound which can form a photosensitive silver halide after reaction with said silver carboxylate, (3) as a reducing agent, a compound which can reduce said silver carboxylate to form silver images, when heated in the presence of sensitized silver halide, and (4) a binder. 5

10 30. A heat-developable photographic material as claimed in Claim 29, in which the photosensitive layer comprising components 1, 2, 3 and 4, also contains one or more of the following: a blackening agent, a development accelerator, an inorganic hydroxide, a reducing agent and a spectral sensitizing dye. 10

31. A heat-developable photographic material as claimed in Claim 30, substantially as hereinbefore described with reference to any one of Examples 1 to 3.

15 32. Photographs produced by imagewise exposing and thermally developing a material as claimed in any of Claims 29 to 31. 15

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